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(71) Applicant: ASAHI DENKA KOGYO KK

(72) Inventor: GODA TETSUYA
BEPPU KOJI
KOMIYA KAORU

(54) EMULSIFIER FOR WATER-IN-OIL(W/O) TYPE EMULSION POLYMERIZATION AND DISPERSANT FOR SUSPENSION POLYMERIZATION

(57) Abstract:

PROBLEM TO BE SOLVED: To obtain an emulsifier for water-in-oil(W/O) type emulsion polymerization having good emulsion stability and a dispersant for suspension polymerization, a water-in-oil(W/O) type resin emulsion having good emulsion stability, and to provide a method for polymerizing a water absorbing resin by water-in-oil(W/O) type emulsion polymerization having good emulsion stability.

SOLUTION: This water-in-oil(W/O) type emulsifier for emulsion polymerization or this dispersant for suspension polymerization is a compound expressed by the general formula R1-O-(AO)nX (1) (where R1 represents a linear, secondary or branched alkyl group, an alkenyl group, a phenyl group or an alkylphenyl group having 1 to 36 carbons; A represents two or more selected from the group consisting of an ethylene group, a propylene group, a butylene group and a styrene group excluding the case in which only two kinds of an ethylene group and a butylene group are combined; X represents an anionic hydrophilic group; and n is a number of 2 to 200).

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(71)Applicant : ASAHI DENKA KOGYO KK
(72)Inventor : GODA TETSUYA
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PROBLEM TO BE SOLVED: To obtain an emulsifier for water-in-oil(W/O) type emulsion polymerization having good emulsion stability and a dispersant for suspension polymerization, a water-in-oil(W/O) type resin emulsion having good emulsion stability, and to provide a method for polymerizing a water absorbing resin by water-in- oil(W/O) type emulsion polymerization having good emulsion stability.
SOLUTION: This water-in-oil(W/O) type emulsifier for emulsion polymerization or this dispersant for suspension polymerization is a compound expressed by the general formula R1-O-(AO)nX (1) (where R1 represents a linear, secondary or branched alkyl group, an alkenyl group, a phenyl group or an alkylphenyl group having 1 to 36 carbons; A represents two or more selected from the group consisting of an ethylene group, a propylene group, a butylene group and a styrene group excluding the case in which only two kinds of an ethylene group and a butylene group are combined; X represents an anionic hydrophilic group; and n is a number of 2 to 200).

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* NOTICES *

1. This document has been translated by computer.So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]
[Claim 1] The emulsifier for the water-type (W/O type) emulsion polymerizations in an oil characterized by being the compound expressed with the following general formula (1).
[Formula 1] R1-O-(AO)nX (1)
(R1 shows the straight chain of carbon numbers 1-36, the 2nd class or the alkyl group of branching, an ARUKENIRU machine, a phenyl group, and an alkylphenyl machine, and A shows two or more sorts chosen from an ethylene, a propylene machine, a butylene machine, and a styrene machine (however, an ethylene and a butylene machine accept two kinds, it comes out, and a certain case is removed).) X shows an anionic hydrophilic group and n shows the number of 2-200.
[Claim 2] The emulsifier for the water-type (W/O type) emulsion polymerizations in an oil according to claim 1 characterized by the compound of a general formula (1) being a compound expressed with the following general formula (2).
[Formula 2] R1-O-(R2O)m-(EO)pX (2)
(R1 shows the straight chain of carbon numbers 1-36, the 2nd class or the alkyl group of branching, an ARUKENIRU machine, a phenyl group, and an alkylphenyl machine, R2 shows a propylene machine or a styrene machine, E shows an ethylene, X shows an anionic hydrophilic group, and m and p show one or more numbers, and are m+p=2-200.)
[Claim 3] The emulsifier for the water-type (W/O type) emulsion polymerizations in an oil according to claim 1 characterized by the compound of a general formula (1) being a compound expressed with the following general formula (3) or (4).
[Formula 3]
R1-O-(R3O)q-(R2O)r-(EO)sX (3)
R1-O-(R2O)r-(R3O)q-(EO)sX (4)
(R1 shows the straight chain of carbon numbers 1-36, the 2nd class or the alkyl group of branching, an ARUKENIRU machine, a phenyl group, and an alkylphenyl machine, R2 shows a propylene machine or a styrene machine, R3 shows a butylene machine or a styrene machine, E shows an ethylene, X shows an anionic hydrophilic group, q and r show one or more numbers, and s shows zero or more numbers and is q+r+s=2-200.)
[Claim 4] The dispersant for suspension polymerizations which consists of a claim 1 or an emulsifier for the water-type (W/O type) emulsion polymerizations in an oil of three given in any 1 term.
[Claim 5] The water-type (W/O type) resin emulsion in an oil which carried out the emulsion polymerization with the emulsifier for the water-type (W/O type) emulsion polymerizations in an oil or the dispersant for suspension polymerizations of four a claim 1 or given in any 1 term.
[Claim 6] The polymerization method of the absorptivity resin by the water-type (W/O type) emulsion polymerization in an oil which used the emulsifier for the water-type (W/O type) emulsion polymerizations in an oil or the dispersant for suspension polymerizations of four a claim 1 or given in any 1 term.

[Translation done.]

* NOTICES *

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] this invention relates to the emulsifier for the water-type (W/O type) emulsion polymerizations in an oil, and the dispersant for suspension polymerizations.
[0002]
[Description of the Prior Art] Conventionally, as the emulsifier for the water-type (W/O type) emulsion polymerizations in an oil, or a dispersant for suspension polymerizations, surfactants, such as a polyoxyethylene type of Nonion systems, such as sorbitan monochrome olate and polyoxyethylenesorbitan monostearate, an ethanolamine type, and a polyethylene-glycol type, an oil-soluble cellulose ester, a cellulose ether, etc. are used. The emulsifier for emulsion polymerizations or the dispersant for suspension polymerizations participates in the initiation reaction and the generation reaction of a polymerization, it participates in the mechanical stability of the emulsion generated further, chemical stability, freeze thaw stability, storage stability, etc., and having big influence on the physical properties of the polymerization object obtained further is known. There was conventionally excellent nothing in the emulsifier for the water-type (W/O type) emulsion polymerizations in an oil or the dispersant for suspension polymerizations used when performing the water-type (W/O type) emulsion polymerization in an oil especially, and especially the emulsion stability had become a problem.
[0003] On the other hand, the absorptivity resin is widely used for industrial ways, such as not only hygienic goods, such as a disposable diaper and sanitary items, but a water cutoff agent, a dew condensation inhibitor, a freshner, a solvent dehydrating agent, etc., tree planting, the plantation art use, etc., and various absorptivity resins are proposed in recent years. For example, various kinds of things, such as a carboxymethyl-cellulose (CMC) bridge formation object, bridge formation polyacrylic-acid (salt), and acrylic-acid (salt)-vinyl alcohol copolymer and a bridge formation polyethylene oxide, are known. When obtaining these absorptivity resins, the water-type (W/O type) emulsion-polymerization method in an oil is performed. For example, the example which used the nonionic surface active agent of HLB 6-9 for JP,57-167302,A, and used the surfactant of HLB 8-12 for JP,60-25045,B is reported to JP,54-30710,B in the sorbitan fatty acid ester as an emulsifier. However, when the water-type (W/O type) emulsion polymerization in an oil was performed using the emulsifier or dispersant of these former, emulsion stability was bad, there is nothing that can acquire the emulsification state which satisfaction can do, and the emulsifier for the water-type (W/O type) emulsion polymerizations in an oil or the dispersant for suspension polymerizations in which does not go and the absorptivity resin naturally obtained was also satisfactorily excellent was desired.
[0004]
[Problem(s) to be Solved by the Invention] Therefore, the purpose of this invention is offering the emulsifier for the water-type (W/O type) emulsion polymerizations in an oil and the dispersant for suspension polymerizations with which the water-type (W/O type) emulsification object in an oil with good emulsion stability is obtained. Moreover, the purpose of this invention is to offer the water-type (W/O type) resin emulsion in an oil with good emulsion stability. Furthermore, the purpose of this invention is to offer the polymerization method of the absorptivity resin by the water-

type (W/O type) emulsion polymerization in an oil with good emulsion stability.
[0005]
[Means for Solving the Problem] This invention persons found out that the compound of the following general formula (1) was excellent as the emulsifier for the water-type (W/O type) emulsion polymerizations in an oil, or a dispersant for suspension polymerizations, as a result of repeating research wholeheartedly.
[0006] That is, the emulsifier for the water-type (W/O type) emulsion polymerizations in an oil characterized by this invention being a compound expressed with the following general formula (1) is offered.
[0007]
[Formula 4] R1-O-(AO)nX (1)
[0008] (R1 shows the straight chain of carbon numbers 1-36, the 2nd class or the alkyl group of branching, an alkenyl machine, a phenyl group, and an alkylphenyl machine, and A shows two or more sorts chosen from an ethylene, a propylene machine, a butylene machine, and a styrene machine (however, an ethylene and a butylene machine accept two kinds, it comes out, and a certain case is removed).) X shows an anionic hydrophilic group and n shows the number of 2-200.
[0009] Moreover, this invention offers the aforementioned emulsifier for the water-type (W/O type) emulsion polymerizations in an oil characterized by the compound of a general formula (1) being a compound expressed with the following general formula (2).
[0010]
[Formula 5] R1-O-(R2O)m-(EO)pX (2)
[0011] (R1 shows the straight chain of carbon numbers 1-36, the 2nd class or the alkyl group of branching, an alkenyl machine, a phenyl group, and an alkylphenyl machine, R2 shows a propylene machine or a styrene machine, E shows an ethylene, X shows an anionic hydrophilic group, and m and p show one or more numbers, and are m+p=2-200.)
[0012] Moreover, this invention offers the aforementioned emulsifier for the water-type (W/O type) emulsion polymerizations in an oil characterized by the compound of a general formula (1) being a compound expressed with the following general formula (3) or (4).
[0013]
[Formula 6]
R1-O-(R3O)q-(R2O)r-(EO)sX (3)
R1-O-(R2O)r-(R3O)q-(EO)sX (4)
[0014] (R1 shows the straight chain of carbon numbers 1-36, the 2nd class or the alkyl group of branching, an alkenyl machine, a phenyl group, and an alkylphenyl machine, R2 shows a propylene machine or a styrene machine, R3 shows a butylene machine or a styrene machine, E shows an ethylene, X shows an anionic hydrophilic group, q and r show one or more numbers, and s shows zero or more numbers and is q+r+s=2-200.)
[0015] Moreover, this invention offers the dispersant for suspension polymerizations which consists of the aforementioned emulsifier for the water-type (W/O type) emulsion polymerizations in an oil.
[0016] Moreover, this invention offers the water-type (W/O type) resin emulsion in an oil which carried out the emulsion polymerization with the aforementioned emulsifier for the water-type (W/O type) emulsion polymerizations in an oil, or the dispersant for suspension polymerizations.
[0017] Moreover, this invention offers the polymerization method of the absorptivity resin by the water-type (W/O type) emulsion polymerization in an oil which used the aforementioned emulsifier for the water-type (W/O type) emulsion polymerizations in an oil, or the dispersant for suspension polymerizations.
[0018]
[Embodiments of the Invention] The emulsifier for the water-type (W/O type) emulsion polymerizations in an oil or the dispersant for suspension polymerizations of this invention is a compound expressed with the following general formula (1).
[0019]
[Formula 7] R1-O-(AO)nX (1)
[0020] (R1 shows the straight chain of carbon numbers 1-36, the 2nd class or the alkyl group of branching, an alkenyl machine, a phenyl group, and an alkylphenyl machine, and A shows two or

more sorts chosen from an ethylene, a propylene machine, a butylene machine, and a styrene machine (however, an ethylene and a butylene machine accept two kinds, it comes out, and a certain case is removed).) X shows an anionic hydroxyl group and n shows the number of 2-200.
[0021] Among a formula (1), R1 is the residue of the monovalent hydroxy compound of carbon numbers 1-36, and is a straight chain, the 2nd class or the alkyl group of branching, an alkenyl machine, a phenyl group, and an alkylphenyl machine. As an example of the monovalent hydroxy compound, as monovalent alcohol For example, a methanol, ethanol, propanol, 2-propanol, A butanol, a pentanol, a hexanol, a heptanol, an octanol, 2-ethyl hexanol, nonanol, a decanol, lauryl alcohol, A tridecanol, an iso tridecyl alcohol, a myristyl alcohol, Cetyl alcohol, palmityl alcohol, a stearyl alcohol, Eicosa Norian, docosa Norian, tetracosa Norian, the hexacosanol, OKUTAKOSA Norian, a myricyl alcohol, a RASSE roll, tetrapod thoria contour Norian, A behenyl alcohol, allyl alcohol, oleyl alcohol, isostearyl alcohol, A cyclopentanol, a cyclohexanol, 2-butyl octanol, 2-butyl decanol, 2-hexyl dodecanol, 2-hexyl decanol, 2-octyl decanol, 2-octyl dodecanol, 2-desyl tetrapod decanol, etc. are mentioned. As a still more nearly monovalent phenol, a phenol, cresol, ethylphenol, tertiary butylphenol, an octyl phenol, a nonyl phenol, a dodecyl phenol, a styrene-ized phenol, a PARAKU mill phenol, etc. are mentioned. In these monovalent hydroxy compounds, the monohydric alcohol of the straight chain of carbon numbers 1-24, the 2nd class, or branching is desirable. That is, R1 has desirable carbon numbers 1-24.
[0022] Although A shows two or more sorts which consist of an ethylene, propylene machines, butylene machines, and styrene machines among a general formula (1) An ethylene and a butylene machine accept two kinds, it comes out, and a certain case is removed. AO in a general formula (1) It is what carried out the addition polymerization of the two or more sorts chosen from an ethyleneoxide (EO), propylene oxide (PO), butylene oxide (1, 2-butylene oxide) (BO), and styrene oxide (StO). You may be a random polymerization, block polymerization, or random/block copolymerization, and block polymerization is desirable especially. It is the number of addition mols, and n is 2-200 and 15-80 are desirable.
[0023] Moreover, among a general formula (1), X shows an anionic hydrophilic group and the basis expressed with following general formula (5) - (8) is mentioned as the example.
[0024]
[Formula 8] -SO3M (5)
[0025] (M shows a hydrogen atom, an alkali-metal atom, ammonium, pyridinium, an alkanolamine, or an alkylamine.)
[0026]
[Formula 9] -PO3M (6)
[0027] (M shows a hydrogen atom, an alkali-metal atom, ammonium, pyridinium, an alkanolamine, or an alkylamine.)
[0028]
[Formula 10] -CH2COOM (7)
[0029] (M shows a hydrogen atom, an alkali-metal atom, ammonium, pyridinium, an alkanolamine, or an alkylamine.)
[0030]
[Formula 11] -CO-R4-COOM (8
[0031] (R4 shows the residue excluding the carboxyl group from the NI base acid, and M shows a hydrogen atom, an alkali-metal atom, ammonium, pyridinium, an alkanolamine, or an alkylamine.) Among these, the basis of a general formula (5), (6), and (7) is desirable, and especially the basis of a general formula (5) is desirable. Sodium, ammonium, and the diethanolamine of M are desirable and especially its sodium and ammonium are desirable.
[0032] It is the compound expressed with the general formula (1) of this invention, and a desirable compound is a compound expressed with a general formula (2).
[0033]
[Formula 12] R1-O-(R2O)m-(EO)pX (2)
[0034] (R1 shows the straight chain of carbon numbers 1-36, the 2nd class or the alkyl group of branching, an alkenyl machine, a phenyl group, and an alkylphenyl machine, R2 shows a propylene machine or a styrene machine, E shows an ethylene, X shows an anionic hydrophilic group, and m

and p show one or more numbers, and are m+p=2-200.)
[0035] Among a formula (2), R1 is the same as that of the above-mentioned general formula (1), and X of it is the same as that of the above-mentioned general formula (1). R2 is a propylene machine or a styrene machine among a formula (2), and E is an ethylene. That to which R2O in a general formula (2) carried out propylene oxide (PO) or styrene oxide (StO), and EO carried out the addition polymerization of the ethyleneoxide (EO) is shown, a polymerization may be a random polymerization, block polymerization, or random/block copolymerization, and its block polymerization is desirable especially. m and p are each number of addition mols, m and p show one or more numbers, and the sum totals of m+p are 2-200. As for m, 20-45 are desirable, and, as for p, 1-20 are desirable.
[0036] Moreover, it is the compound expressed with the general formula (1) of this invention, and a desirable compound is a compound expressed with a general formula (3) or (4).
[0037]
[Formula 13]
R1-O-(R3O)q-(R2O)r-(EO)sX (3)
R1-O-(R2O)r-(R3O)q-(EO)sX (4)
[0038] (R1 shows the straight chain of carbon numbers 1-36, the 2nd class or the alkyl group of branching, an alkenyl machine, a phenyl group, and an alkylphenyl machine, R2 shows a propylene machine or a styrene machine, R3 shows a butylene machine or a styrene machine, E shows an ethylene, X shows an anionic hydrophilic group, q and r show one or more numbers, and s shows zero or more numbers and is q+r+s=2-200.)
[0039] Among a formula (3) or (4), R1 is the same as that of the above-mentioned general formula (1), and X of it is the same as that of the above-mentioned general formula (1). R3 is a butylene machine or a styrene machine among a formula (3) or (4), R2 is a propylene machine or a styrene machine, and E is an ethylene. R3O in a general formula (3) or (4) shows that to which R2O carried out propylene oxide (PO) or styrene oxide (StO), and EO carried out the addition polymerization of the ethyleneoxide (EO) for butylene oxide (BO) or styrene oxide (StO), a polymerization may be a random polymerization, block polymerization, or random/block copolymerization, and its block polymerization is desirable especially. q, r, and s are each number of addition mols, q and r show one or more numbers, s shows zero or more numbers, and the sum totals of q+r+s are 2-200. As for q, 15-40 are desirable, as for r, 1-25 are desirable, and, as for s with more desirable 5-25, 0-15 are desirable.
[0040] The manufacture method of a compound expressed with a general formula (1) To the above and a monovalent hydroxy compound, an ethyleneoxide (EO), propylene oxide (PO), The addition polymerization reaction of the two or more (however, the case where they are two kinds, BO and EO, is removed) sorts in butylene oxide (1, 2-butylene oxide) (BO) and styrene oxide (StO) is carried out. What is necessary is to make the hydroxyl of the obtained polyether monochrome all compound into an anionic hydrophilic group, and just to neutralize it by the conventional method, according to the purpose compound.
[0041] For example, when making it the -SO3M set of the aforementioned general formula (5), a sulfating agent can be made to be able to react to the obtained polyether monochrome all compound, and it can obtain by neutralizing if needed. What is necessary is to mention well-known sulfating agents, such as a chlorosulfonic acid, sulfuric anhydride, and a sulfamic acid, and just to use alkylamines, such as alkanolamines, such as alkali-metal hydroxides, such as a sodium hydroxide and a potassium hydroxide, ammonia, a pyridine, a monoethanolamine, a diethanolamine, and a triethanolamine, a monoethyl amine, a diethylamine, and a triethylamine, etc. as an example of a sulfating agent, when neutralizing.
[0042] Similarly, when making it the -PO3M set of the aforementioned general formula (6), a phosphorus pentaoxide, polyphosphoric acid, etc. can be used for the obtained polyether monochrome all compound, and it can phosphoric-ester-ize by the conventional method, and can obtain by neutralizing if needed. What is necessary is just to use alkylamines, such as alkanolamines, such as alkali-metal hydroxides, such as a sodium hydroxide and a potassium hydroxide, ammonia, a pyridine, a monoethanolamine, a diethanolamine, and a triethanolamine, a monoethyl amine, a diethylamine, and a triethylamine, etc., when neutralizing.

[0043] Similarly, when making it the -CH2COOM basis of the aforementioned general formula (7), the chloroacetic acid etc. can be used for the obtained polyether monochrome all compound, and it can be made to be able to react by the conventional method, and can obtain by neutralizing if needed. What is necessary is just to use alkylamines, such as alkanolamines, such as alkali-metal hydroxides, such as a sodium hydroxide and a potassium hydroxide, ammonia, a pyridine, a monoethanolamine, a diethanolamine, and a triethanolamine, a monoethyl amine, a diethylamine, and a triethylamine, etc., when neutralizing.

[0044] Similarly, when making it the -CO-R4-COOM basis of the aforementioned general formula (8), a dibasic acid or its anhydride can be made to be able to react to the obtained polyether monochrome all compound by the conventional method, and it can obtain by neutralizing if needed. As an example of a dibasic acid, for example Oxalic acid, a malonic acid, a succinic acid, a glutaric acid, An adipic acid, a pimelic acid, a suberic acid, an azelaic acid, a sebacic acid, Saturated-fat group dicarboxylic acids, such as undecane diacid, dodecane diacid, a tridecanedioic acid, and tetradecane diacid, Saturation alicycle group dicarboxylic acids, such as a cyclopentane dicarboxylic acid, hexahydrophthalic acid, and methyl hexahydrophthalic acid, Aromatic dicarboxylic acids, such as a phthalic acid, an isophthalic acid, a terephthalic acid, a tolylene dicarboxylic acid, and a xylylene dicarboxylic acid, Unsaturation aliphatic dicarboxylic acids, such as a maleic acid, a fumaric acid, an itaconic acid, a citraconic acid, and a mesaconic acid, A tetrahydrophtal acid, a methyl tetrahydrophtal acid, a NAJIKKU acid (and methylene tetrahydrophtal acid), Unsaturation alicycle group dicarboxylic acids, such as a methyl NAJIKKU acid, a methyl butenyl tetrahydrophtal acid, and a methyl pentenyl tetrahydrophtal acid, etc. are mentioned. as an example of an anhydride These anhydrides are mentioned, and when neutralizing Alkali-metal hydroxides, such as a sodium hydroxide and a potassium hydroxide, ammonia, What is necessary is just to use alkylamines, such as alkanolamines, such as a pyridine, a monoethanolamine, a diethanolamine, and a triethanolamine, a monoethyl amine, a diethylamine, and a triethylamine, etc. When the product obtained by the above-mentioned method contains an unreacted object, a by-product, etc., it remains as it is and can also use, and naturally, a well-known refining means can refine and it can also use.

[0045] The emulsifier for the water-type (W/O type) emulsion polymerizations in an oil or the dispersant for suspension polymerizations of this invention can obtain the water-type (W/O type) emulsification object in an oil with good emulsion stability. Especially, it excels in the use to the water-type (W/O type) emulsion polymerization in an oil, and the water-type (W/O type) resin emulsion in an oil excellent in emulsion stability can be obtained. Furthermore, it excels in the use to the water-type (W/O type) emulsion polymerization in an oil of an absorptivity resin.

[0046] The polymerization system suitable for using the emulsifier for the water-type (W/O type) emulsion polymerizations in an oil or the dispersant for suspension polymerizations of this invention Are the radical polymerization system of the water-type (W/O type) emulsion polymerization in an oil, or the water-type (W/O type) suspension polymerization in an oil, and the emulsifier for the water-type (W/O type) emulsion polymerizations in an oil or the dispersant for suspension polymerizations of this invention is used. It is suitable for manufacture of the homopolymer or copolymer which consists of a monomer illustrated below preferably that what is necessary is just to form the emulsification state of the water type in an oil (W/O type).

[0047] For example, vinyl acetate, a propionic-acid vinyl, alkyl vinyl ether, Vinyl compounds, such as an alkyl vinyl ketone, an acrylic acid, a methyl acrylate, A methyl methacrylate, a butyl acrylate, acrylic-acid 2-ethylhexyl, Acrylic compounds, such as metaglycidyl acrylate, acrylonitrile, and an acrylamide, Aromatic vinyl compounds, such as styrene, an alpha methyl styrene, and vinyltoluene, Ethylene, a propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, 1-undecene, Alpha olefin compounds, such as 1-dodecen, 1-tridecenoic, and 1-tetrapod decene, Conjugated dienes, such as a butadiene, an isoprene, and a pentadiene, a vinyl chloride, Halogenation olefin compounds, such as a vinylidene chloride, a maleic anhydride, Maleates, itaconic-acid ester, an acrylonitrile-butadiene-styrene latex (ABS latex), a styrene-butadiene latex (SBR latex), an acrylic emulsion, an acrylic-styrene system emulsion, etc. are mentioned.

[0048] Furthermore, especially the emulsifier for the water-type (W/O type) emulsion polymerizations in an oil or the dispersant for suspension polymerizations of this invention is suitable for the water-type (W/O type) emulsion polymerization in an oil of an absorptivity resin, or

the water-type (W/O type) suspension polymerization in an oil, and as long as it is an absorptivity resin, which thing is sufficient as it, and it is suitable for manufacture of the absorptivity resin which is the homopolymer which consists of a monomer illustrated below, or a copolymer.
[0049] For example, an acrylic acid (meta) and/or its alkali-metal salt, an ammonium salt, ionicity monomer [, such as a 2-(meta)-acrylamide-2-methyl sulfonic acid and/or its alkali-metal salt,]; -- acrylic-esters [, such as acrylic-acid 2-ethylhexyl,] (meta); -- styrene-monomer; (meta) -- acrylamide, N, and N-dimethyl acrylamide -- Non-ionicity monomers, such as 2-hydroxyethyl (meta) acrylate and N MECHIRORU (meta) acrylamide; Diethylaminoethyl (meta) acrylate, Amino-group content unsaturation monomers, the 4th class ghosts of those, etc., such as dimethylamino propyl (meta) acrylate, can be mentioned, and a kind chosen from these groups or two sorts or more can be used. In addition, the term a "(meta)acrylic" shall mean both an "acrylic" and "methacrylic one" here.
[0050] What is necessary is just to perform the water-type (W/O type) emulsion polymerization in an oil, or a suspension polymerization for the aforementioned monomer etc. by the conventional method using the emulsifier for the water-type (W/O type) emulsion polymerizations in an oil or the dispersant for suspension polymerizations of this invention, when manufacturing the aforementioned absorptivity resin. For example, what is necessary is to add and heat a polymerization initiator to the water-type (W/O type) resin emulsion in an oil containing a monomer, and just to perform polymerization reaction.
[0051] When obtaining the water-type (W/O type) resin emulsion in an oil, or an absorptivity resin by this invention, in the range which does not spoil the effect of this invention in the water-type (W/O type) emulsion-polymerization system in an oil It is the polyfunctional monomer which the cross linking agent may be contained if needed and may copolymerize a cross linking agent. for example, JI of a divinylbenzene and polyhydric alcohol and a TORI (meta) acrylic ester (ethylene glycol diacrylate --) An allyl compound, methylene screw acrylamides (a diallyl phthalate, allyl-compound acrylate, triallyl isocyanurate, etc.), etc., such as ethylene glycol dimethacrylate and triethylene-glycol dimethacrylate, are mentioned.
[0052] Although the amount of the emulsifier for the water-type (W/O type) emulsion polymerizations in an oil of this invention or the dispersant for suspension polymerizations used can be conventionally used arbitrarily in the range of the amount of anticipated use of the well-known emulsifier for emulsion polymerizations, or a dispersant, 0.2 - 10 % of the weight is preferably good [the amount] 0.1 to 20% of the weight to a raw material monomer in general. Moreover, the combined use with this compound, other emulsifiers, or a dispersant is also possible in the range by which the effect of this invention is not spoiled.
[0053] As an example of the polymerization initiator when using the emulsifier for the water-type (W/O type) emulsion polymerizations in an oil or the dispersant for suspension polymerizations of this invention for an emulsion polymerization and a suspension polymerization That what is necessary is just what is used usually, as the example Persulfates, such as a hydrogen peroxide, potassium persulfate, a sodium persulfate, and an ammonium persulfate, - azobis -(2-amidinopropane) 2 hydrochloride and 2 and 2 '2, 2'-azobis -(N and N'-dimethylene isobutyl amidine) 2 hydrochloride, They are azo system initiators, such as 2 and 2'-azobis {a 2 methyl-N-[1 and 1-screw (hydroxymethyl)-2-hydroxyethyl] propione amide} and an azobisisobutyronitril. You may mix and use these. Moreover, a hydrogen peroxide and a persulfate can be used also as an initiator of a redox type combining reducing matter, amines, etc., such as a sulfite and L ascorbic acid.
[0054]
[Example] Hereafter, this invention is not limited by these examples although an example explains this invention concretely.
[0055] The example 1 <manufacture of emulsifier for W/O type emulsion polymerizations or dispersant for suspension polymerizations> methanol was able to be made to have been able to carry out the addition polymerization (block polymerization) reaction of an ethyleneoxide (EO), propylene oxide (PO), and the butylene oxide (BO), the chlorosulfonic acid was able to be made to have been able to react to it as a sulfating agent at the obtained polyether methanol compound, and this invention article 1 was able to be obtained by neutralizing with ammonia. The suitable reagent was used for examples 2-13 based on the structure of the emulsifier shown in Table 1, they performed

each reaction by the same method as the above, and manufactured this invention article 2-13.
[0056] While making it dissolve in the monomer (acrylic-acid-2-ethylhexyl, styrene, acrylic acid) of each loadings of the following table 2 (I) and stirring the emulsifier of this invention article 1-13 of the <W/O type emulsion stability examination> following table 1, and the comparison article 1-2 10g of CaCl(s)2 of the following table 2 (II) was dissolved in it, it heated at 70 degrees C, and 200g of water of the following table 2 (II) was added. 30-minute stirring after a dropping end of water was continued, the water-type (W/O type) resin emulsion in an oil was obtained, and viewing estimated emulsion stability on the following criteria. A result is shown in Table 3.
[0057] (Emulsion stability evaluation)
O :W/O type emulsification object (with no separation of a water layer).
O : although there is separation of a water layer a little, it is an W/O type emulsification object.
x: Dissociate completely (it has not emulsified to an W/O type).
[0058]
[Table 1]

		乳化剤の構造 R^1-O-(AO)$_n$X			
		ベースアルコール (R^1-O-)	(AO)$_n$	重合形態	X
本発明品	1	C1(メタノール)	$(BO)_{25}$-$(PO)_1$-$(EO)_5$	ブロック	SO_3NH_4
	2	C2(エタノール)	$(BO)_{70}$-$(PO)_{10}$-$(EO)_5$	ブロック	SO_3Na
	3	C4(n-ブタノール)	$(BO)_{33}$-$(PO)_5$-$(EO)_{10}$	ブロック	SO_3Na
	4	C4(n-ブタノール)	$(BO)_{39}$-$(PO)_5$	ブロック	SO_3NH_4
	5	C8(直鎖)	$(PO)_{10}$-$(BO)_{20}$	ブロック	SO_3NH_4
	6	C10(分岐)	$(BO)_{70}$-$(PO)_{20}$-$(EO)_5$	ランダム	PO_3Na
	7	C12(2級)	$(BO)_{24}$-$(PO)_{10}$-$(EO)_{10}$	ブロック	CH_2COONa
	8	C12(2級)	$(BO)_{15}$-$(PO)_{10}$	ブロック	SO_3Na
	9	C16(分岐)	$(PO)_{20}$-$(EO)_{10}$	ランダム	$SO_3NH_3(C_2H_4OH)_3$*1
	10	C18(分岐)	$(StO)_{20}$-$(EO)_{20}$	ブロック	SO_3NH_4
	11	C18(分岐)	$(PO)_5$-$(BO)_{20}$	ブロック	SO_3NH_4
	12	C20(直鎖)	$(PO)_{30}$-$(EO)_5$	ブロック	SO_3Na
	13	C24(分岐)	$(PO)_{25}$-$(EO)_3$	ブロック	SO_3NH_4
比較品1		$C_{12}H_{25}$-$(EO)_4$-OH			
比較品2		$C_{16}H_{33}$-$(EO)_3$-OH			

＊表中、Cに続く数字はアルコールの炭素数を示す。
＊表中、直鎖は直鎖アルコールを、分岐は分岐アルコールを、
2級は2級アルコールを示す。
＊表中、ブロックはブロック重合を、ランダムはランダム重合を示す。
＊1：スルホン酸基のジエタノールアミン塩を示す。

[0059]
[Table 2]

	配合物	配合量(g)
I	本発明品及び比較品の各乳化剤	0.2
	アクリル酸－2－エチルヘキシル	5
	スチレン	1
	アクリル酸	0.1
II	$CaCl_2$	5
	イオン交換水	150
	合計	161.3

[0060] 0.09g [of potassium persulfate] and azobisisobutyronitril 0.09g was added to the water-type (W/O type) resin emulsion in an oil obtained by the <emulsion-polymerization test> above as a polymerization initiator, and it mixed for 30 minutes, and moved to the mortar. It was heated by the 70-degree C thermostat for 20 hours, it dried at 105 more degrees C for 3 hours, moisture was removed, and the emulsion-polymerization object was obtained. Viewing estimated the appearance of an emulsion-polymerization object on the following criteria. A result is shown in Table 3.
[0061] (Emulsion-polymerization evaluation)
O : the foamy polymerization object was obtained.
x: A polymerization has not been carried out.
[0062]
[Table 3]

		W／O型乳化安定性試験	乳化重合試験
本発明品	1	◎	○
	2	◎	○
	3	◎	○
	4	○	○
	5	○	○
	6	◎	○
	7	◎	○
	8	○	○
	9	◎	○
	10	◎	○
	11	○	○
	12	◎	○
	13	◎	○
比較品	1	×	−
	2	×	−

[0063]
[Effect of the Invention] According to this invention, the polymerization method of the absorptivity resin by the emulsifier for the water-type (W/O type) emulsion polymerizations in an oil with which the water-type (W/O type) emulsification object in an oil with good emulsion stability is obtained and the dispersant for suspension polymerizations, the water-type (W/O type) resin emulsion in an oil with good emulsion stability, and the water-type (W/O type) emulsion polymerization in an oil with good emulsion stability is offered.

[Translation done.]

* NOTICES *

EXAMPLE

[Example] Hereafter, this invention is not limited by these examples although an example explains this invention concretely.
[0055] The example 1 <manufacture of emulsifier for W/O type emulsion polymerizations or dispersant for suspension polymerizations> methanol was able to be made to have been able to carry out the addition polymerization (block polymerization) reaction of an ethyleneoxide (EO), propylene oxide (PO), and the butylene oxide (BO), the chlorosulfonic acid was able to be made to have been able to react to it as a sulfating agent at the obtained polyether methanol compound, and this invention article 1 was able to be obtained by neutralizing with ammonia. The suitable reagent was used for examples 2-13 based on the structure of the emulsifier shown in Table 1, they performed each reaction by the same method as the above, and manufactured this invention article 2-13.
[0056] While making it dissolve in the monomer (acrylic-acid-2-ethylhexyl, styrene, acrylic acid) of each loadings of the following table 2 (I) and stirring the emulsifier of this invention article 1-13 of the <W/O type emulsion stability examination> following table 1, and the comparison article 1-2 10g of CaCl(s)2 of the following table 2 (II) was dissolved in it, it heated at 70 degrees C, and 200g of water of the following table 2 (II) was added. 30-minute stirring after a dropping end of water was continued, the water-type (W/O type) resin emulsion in an oil was obtained, and viewing estimated emulsion stability on the following criteria. A result is shown in Table 3.
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[0058]
[Table 1]

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	3	C4(n-ブタノール)	$(BO)_{23}$-$(PO)_5$-$(ED)_{10}$	ブロック	SO_3Na
	4	C4(n-ブタノール)	$(BO)_{20}$-$(PO)_1$	ブロック	SO_3NH_4
	5	C8(直鎖)	$(PO)_{11}$-$(BO)_{20}$	ブロック	SO_3NH_4
	6	C10(分岐)	$(BO)_{24}$-$(PO)_{20}$-$(EO)_5$	ランダム	PO_3Na
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	11	C18(分岐)	$(PO)_5$-$(BO)_{20}$	ブロック	SO_3NH_4
	12	C20(直鎖)	$(PO)_{30}$-$(EO)_5$	ブロック	SO_3Na
	13	C24(分岐)	$(PO)_{45}$-$(EO)_3$	ブロック	SO_3NH_4
比較品 1		$C_{18}H_{35}$-$(EO)_4$-OH			
比較品 2		$C_{16}H_{33}$-$(EO)_2$-OH			

*表中、Cに続く数字はアルコールの炭素数を示す。
*表中、直鎖は直鎖アルコールを、分岐は分岐アルコールを、
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	6	◎	○
	7	◎	○
	8	○	○
	9	◎	○
	10	◎	○
	11	○	○
	12	◎	○
	13	◎	○
比較品	1	×	－
	2	×	－

[Translation done.]